1217035

(54) A METHOD FOR CONTROLLING THE OXIDATION OF CARBOHYDRATES OR POLYHYDRIC ALCOHOLS

(71) We, POLITECHNIKA SLASKA IM. W. PSTROWSKIEGO of W Gliwicach, Poland, a State Enterprise organized under the laws of Poland, do hereby declare the invention
5 for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to a process
10 for the production of monocarboxylic acids which are the first acidic products of the oxidation of carbohydrates or polyhdric alcohols.

The oxidation of polyols or carbohydrates
15 is a complex process yielding numerous non-acidic substances as well as mono- and dicarboxylic acids.

This abundance of products in the post-reaction mixture is a result of a chain of
20 successive reactions and side-reactions.

Previously proposed methods of preparing said monocarboxylic acids relate to batch treatment of the carbohydrates with oxidizing agents in the stoichiometric ratio or higher
25 in order to obtain a complete oxidation of the starting organic materials.

Previously proposed processes using fermentation oxidation are carried out until the starting materials are completely oxidized.
30 The desired product is then isolated from the reaction mixture as a sparingly-soluble salt.

It is also known to purify the post-reaction solution by means of passing the solution
35 through a cation exchange bed, or by sorption of the acidic products of the oxidation in an anion-exchange bed followed by elution there from with a mineral acid or a solution of an alkali.

40 However, the previously proposed processes for producing the said monocarboxylic acids show many disadvantages, for example, the post-oxidation mixtures in general have a complicated chemical composition, due to super-

oxidation of a part of the product which makes 45 it difficult to isolate and purify the desired product from the considerable quantities of by-products and decomposition products. In microbiological oxidation methods, the rate of the batch process is very long and, further- 50 more, the necessity of grafting every successive batch with bacteria involves additional troubles.

Another disadvantage of previously proposed processes is that they are time con- 55 suming operations involving laborious isolation procedures to obtain the desired product.

The low efficiency characterising these known methods of producing the said organic acids is especially evident in the case of 60 L-sorbose oxidation in order to obtain 2 - keto - L - gulonic acid, an intermediate in vitamin C synthesis. The direct oxidation of L-sorbose with nitric acid provides only 5 to 20% of the theoretical yield. In the fer- 65 mentation method of preparing this acid from sorbitol or from L-sorbose, the yield is higher but also insufficient for production on an industrial scale. This method and also the fermentation processes of producing lactic 70 or gluconic acids are lengthy and trouble-some.

It is an object of the present invention to obviate or mitigate the aforesaid disadvantages. 75

According to the present invention there is provided a method of controlling the oxidation of a carbohydrate or polyhydric alcohol comprising treating a feedstock containing the carbohydrate or polyhydric alcohol with an 80 oxidising agent to form a reaction mixture containing a monocarboxylic acid; and removing the monocarboxylic acid during formation thereof so that the feedstock is maintained in the reaction mixture at a con- 85 centration greater than that of the monocarboxylic acid.

Preferably the concentration of the acid

is maintained at a predetermined level related to the oxidation-reduction equipotential point.

Preferably also the acid is removed by means of ion-exchange, electrodialysis or sorption.

In the process according to the invention suitable starting materials are L-sorbose, D-fructose and other ketohexoses, D-glucose, D-mannose and other aldohexoses or aldopentoses, saccharose, lactose or other reducing disaccharides. Furthermore, the technical concentrates and solutions of carbohydrates mentioned above, e.g. starch or cellulose hydrolyzates and molasses or polyhydric alcohols such as sorbitol, mannitol and their analogues can also be used.

The products which may be obtained in the process according to the invention are, for example, 2 - keto - L - gulonic acid and other 2 - keto - hexonic acids, which are valuable intermediates in the synthesis of vitamin C, D-gluconic acid and its analogues, in the form of salts mostly applied in medicine, and lactic acid which is widely used in the food industry.

Any oxidising agent commonly used for the oxidation of carbohydrates and polyhydric alcohols may be used. They are, for example, nitric or nitrous acid or nitrogen oxides, chlorine and bromine or their oxidising acids, having various oxidation states, or their oxidising salts, transition metal salts, hydrogen peroxide solution with a suitable catalyst and also gaseous oxygen, air and other oxygen- or ozone- containing gases, used with or without catalysts.

This process may also be operated using electrochemical oxidation carried out in an electrolyzer, e.g. in the presence of oxygen-carrying media.

As oxidising agents in the process according to the invention, enzymes or bacteria which bring about oxidation of carbohydrates or polyols to organic acids, may be used.

Such bacteria are, for example, Acetobacter, Pseudomonas and Lactobacillus.

However, the selection of a suitable oxidizer does not constitute the subject of this invention.

The removal of the acid product may be effected by ion-exchange. The ion-exchange materials which may be used may be in the form of membranes or ion-exchange resins. Suitable membranes are, for example, Permaplex A-20 and C-20 Zerolit Limited (Trade Marks).

The most suitable cation exchangers are strongly acid polystyrene-sulphonic acid cation-exchangers, for example, Wofatit KPS, Lewalit S, Dowex-50, Amberlite IR-120 (Trade Marks).

As anion exchangers, strongly or medium alkaline anion exchangers, either in polyhydric form or bonded with an anion of a weak acid e.g. carbonic acid are recommended. Suitable resins are, Amberlit IRA-400, Dowex-1, Wofatit SBK, Amberlite IRA-45, Dowex-3 and Wofatit M (Trade Marks).

It was found that in the oxidation of keto-hexoses, a 2 - keto - hexonic acid, firstly formed, is subsequently oxidatively decomposed i.e. it is superoxidized, even though the total keto-hexose was not yet fully reacted. This means that 2 - keto - hexonic acids are stronger reducing agents than the keto-hexoses from which these acids are formed by oxidation.

This phenomenon is especially pronounced when L-sorbose is oxidised to 2 - keto - L - gulonic acid.

The normal oxidation-reduction potential of 2 - keto gulonic acid is much lower than that of L-sorbose and therefore the yield of 2 - keto - L - gulonic acid produced by the hitherto used methods of direct oxidation of L-sorbose, is low. The oxidation-reduction potential of a solution containing feedstock and product changes considerably with a change of the relative concentration of feedstock and product.

10% aqueous solution of L-sorbose shows an rH value of about 20, whereas the same rH value of 2 - keto - L - gulonic acid aqueous solution is obtained at a concentration of approximately 1%. At higher concentrations the reducing properties of the 2 - keto - L - gulonic acid are still higher and the values of the equipotential points with L-sorbose vary with concentration as is shown in the curve in Fig. 1 of the drawings.

Fig. 1 illustrates the dependence of rH value upon the concentration of L-sorbose and 2 - keto - L - gulonic acid.

The concentration/rH curves of the acid are super-imposed onto the concentration/rH curve of the saccharide at three different points, illustrating the initial concentration of the L-sorbose in the reaction mixture. The shifting of equipotential points proves that the higher the initial concentration of saccharide, the greater the proportion of saccharide which can be oxidized to yield 2 - keto - L - gulonic acid. Nevertheless in every case this quantity is only a fraction of the stoichiometric quantity.

In order to prevent the destructive oxidation of the product and to provide a high process efficiency, the acid product should be removed, as soon as possible, preferably in statu nascendi from the reaction mixture. The concentration of the acid is preferably maintained below the concentration indicated by the oxidation-reduction equipotential point.

In removing the oxidation in statu nascendi from the reaction medium, the high rate of formation of the acid product, which as a rule is very high in the first stage of the reaction course, is utilized.

The present invention thus relates to the

continuous partial oxidation of polyhydric alcohols or carbohydrate solutions with the simultaneous removal, preferably in statu nascendi, of the monocarboxylic acids which are the first oxidation products of the said carbohydrate or polyhydric alcohols. The acidic products may be removed from the reaction medium, by, for example electrodialysis through ion-exchange diaphragms, or by their sorption in an ion-exchange bed, and the solution containing the unreacted feedstocks remains in the reaction zone or is recycled therein, whereas the reaction product, i.e. the monocarboxylic acid, is recovered from the far side of the dialyser membrane or is eluted from the ion-exchange bed in a known manner.

A preferred process according to the invention for producing a monocarboxylic acid comprises introducing a small portion of an oxidising agent into a reactor into which a feedstock solution of a carbohydrate or polyhydric alcohol is continuously fed to form a reaction mixture and removing part of the said reaction mixture. The mixture is passed through an ion-exchange column which retains on the resin the acidic product while any unoxidized carbohydrates pass into the effluent, which, together with added feedstocks, is recycled into the reactor. The ion-exchange columns are then regenerated in a known manner by means of a mineral acid or an alkaline solution to yield the solution of the desired acid or a salt thereof.

2 - keto - hexonic acids, or their salts, may be prepared according to the invention by oxidising a ketohexose aqueous solution with a known non-ionic oxidising agent by carrying out the reaction in a reaction medium containing an anion-exchange resin in the hydroxide or carbonate form in an equivalent quantity not lower than the quantity of keto-hexose, which is present in this reaction medium.

The fermentation method according to the invention comprises preparing, for example, 2 - keto - L - gulonic acid by oxidizing sorbitol or L-sorbose with a microbiological oxidising agent in an aqueous solution, carrying out the fermentation process continuously whilst maintaining a substantially constant concentration of the 2 - keto - L - gulonate product and continuously passing a wort from the fermenter through an ion-exchange system wherein the acidic product is retained by sorption, recycling the effluent from the ion exchange unit together with added feedstocks into the fermenter, and eluting the 2 - keto - L - gulonic acid from the ion-exchange bed in a known way.

A process for preparing lactic acid comprises oxidizing a feedstock, which may be sacchrose, molasses, starch or cellulose hydrolyzates individually or in any possible combination, with a microbiological oxidizer, carrying out the fermentation and continuously maintaining a much lower concentration of the product, i.e. of lactate, than the concentration of feedstocks in the fermentation medium, continuously removing a part of the fermentation solution to the ion exchange system, recycling the effluent together with added feedstocks into the fermentation medium and eluating a lactic acid from the ion-exchange columns with a mineral acid in a known way.

Embodiments of the invention will now be described simply by way of example with reference to Figs. 2, 3 and 4 of the accompanying drawings.

Referring to the drawings:

Fig. 2 shows a flow diagram of a first embodiment of the invention and a schematic section of a reactor vessel for use therein;

Fig. 3 shows a flow diagram of a second embodiment of the invention and a schematic section of a reactor vessel for use therein;

Fig. 4 shows a flow diagram of a third embodiment of the invention and a schematic section of a reactor vessel for use therein.

In Fig. 2 the reactor vessel 1 is provided with an anion exchange diaphragm 2, a cation exchange diaphragm 3, an agitator, and electrodes 4 and 5 inducing an electric field according to the ion-exchange diaphragms's characteristics.

Carbohydrate feedstock is continuously fed into the reactor 1 from container 6, and a suitably selected oxidizer from container 7.

An acid is formed in the resultant reaction mixture. This acid migrates, in the induced electric field, towards an anion-exchange diaphragm 2. It then passes through the diaphragm 2 as a solution into the receiver 8.

Cations present in the reaction mixture migrate toward diaphragm 3 through which they penetrate. They then pass in solution into receiver 9.

In use, the rate of removal of the acid from the reaction mixture can be controlled by means of the potential between the electrodes since the rate of diffusion in electrodialysis is dependent upon the potential difference between the electrodes.

Fig. 3 shows a flow diagram of the process and a reactor vessel for use therein when utilizing non-ionic oxidizers, e.g. gaseous oxygen, air or other oxygen-or-ozone-containing gas. The apparatus comprises a column or reactor 1 having a length to diameter ratio of from 1:10 to 1:20. The reactor 1 is provided with a filter partition 2 and a heating-cooling-jacket 3 covering the whole length of the column. A layer of the ion-exchange bed 4 is placed above the filter partition 2, the height thereof being from 4—7 times the reactors column's diameter.

The pipe 6 connects a blower 7 to an outlet pipe 5 positioned below the filter partition 2.

When in use, the carbohydrate feedstock is

fed from the feeder 8 into the reactor 1. Reactor 1 contains a strongly or medium alkaline anion-exchanger in the form of a hydroxide or carbonate together with a suitable catalyst.

An oxygen-carrying gas is simultaneously fed into the reactor by means of a blower 7.

As a result of oxidation occurring in the reaction medium, an organic acid is formed. The acid is bonded to the anion-exchange resin. When the whole ion-exchange bed 4 is saturated, the process is interrupted and the solution is drained away from the reactor 1. The bed 4 is washed with a solvent and subsequently the adsorbed product is eluted using a suitable eluent from the feeder 8.

When a diluted mineral acid is used as the eluent, free organic acid solution is collected in the receiver 9. If a diluted alkaline or salt solution is used as the eluent—a salt solution of an organic acid is collected in the receiver.

The third embodiment shown in Fig. 4 has the most universal usefulness.

The apparatus comprises a reactor 1 which can be of various types depending on the catalyst used e.g. a reactor commonly used in the chemical industry, an electrolyzer for electrochemical oxidation or a fermenting tank for microbiological oxidation. This reactor 1 is connected from its outlet through the filtering means 2 to the cation-exchange column 4. The column 4 is connected to the receiver 5 which also serves as a feeder for the anion-exchange column 6 which in turn is connected to both receivers 7 and 8.

The receiver 7 is connected through pump 9 to preparatory tank 11 which is in turn connected to reactor 1. When reactor 1 is a fermenting tank a sterilizer 3 is provided. Feedstocks and an oxidizer are fed into the reactor 1 where they are mixed and reacted. The reacting solution flows through the filter 2, where solid impurities are mechanically separated by filtration, and into the cation-exchange column 4 where it is freed from metal ions. Subsequently the solution flows into the anion-exchange column 6 where the organic acid included in the solution and other anions derived e.g. from an oxidizer, are bonded.

The solution, freed from the reaction product, passes into the receiver 7 and thereafter into the preparatory tank 11 where new feedstocks are added thereto.

It then flows from tank 11 through the sterilizer 3 into the reactor 1 where it reacts with an oxidizer also flowing therein. From the reactor 1 the solution is processed as described above.

The cation-exchange bed in the column 4 is reactivated with a mineral acid when deactivated. When the anion-exchange bed in the anionic column is fully saturated, the product is eluted therefrom with a dilute mineral acid or with a dilute alkaline or salt solution. When

an alkaline or salt solution is used, an acid salt is obtained in the effluent and additionally in the case of an alkaline solution the bed is simultaneously activated.

When the ion-exchange bed contains not only the adsorbed organic acid (the oxidation product) but also other adsorbed anions derived e.g. from an oxidizer, fractional elution should be used and the desired acid solution collected in the receiver 8 and useless acid solution in another receiver.

The ion-exchange system may be employed for continuous or batch production.

The most profitable results of acid elution are obtained by using an apparatus for industrial sorption processes, with the application of an interstage evacuation of columns.

Use of the aforesaid embodiments is described in the following Examples wherein the quoted percentages and ratios are weight-based.

EXAMPLE 1

A process for the production of 2 - keto - D - gluconic acid. The apparatus shown in Fig. 4 is filled with D - fructose aqueous solution having a 15% concentration. The said solution flows continuously in the direction of the arrows shown in Fig. 4. A 10% solution of permanganic acid is introduced continuously into the reactor 1 at constant flow rate so as to yield a mixture containing considerably less acid than would stoichiometrically be required to oxidise the D - fructose which is flowing through the reactor 1. The ratio of oxidiser to fructose is about 7:100.

The constant concentration of 2 - keto - L - gluconic acid in the reactor is kept constant at about 1.0%.

The solution flowing out from the reactor passes through a pipe to the filter 2 and subsequently into the cation-exchange columns 4.

In these columns, filled with Wofatit KPS cation exchanger in the hydrogen form, the exchange of cation traces to hydrogen ion occurs, and subsequently the solution passes throughout the transitory receivers 5 into the anion-exchange columns 6. The columns 6 are filled with Amberlit IR-45 anion-exchanger in the hydroxide form, wherein 2 - keto - D - gluconic acid is retained while the unreacted D-fructose passes into the effluent.

A portion of the D-fructose which was firstly retained by the anion exchanger 6 is itself displaced as a result of the inflow of subsequent portions of 2 - keto - D - gluconic acid.

D-fructose solution, having a concentration lowered by an oxidized portion bonded in the ion-exchange bed, flows throughout the receivers 7 and the pump 9 to the preparatory tanks 11 wherein fresh d - fructose is simultaneously fed.

The solution then flows from the tanks 11 to the reactor 1 wherein the continuous oxidation occurs.

After a lapse of time the solution flowing out from the anion-exchange column gives an acid reaction.

After diverting the solution flow to pass through another regenerated column, the previous column is washed with water and subsequently 2 - keto - D - gluconic acid is eluted therefrom by washing with hydrochloric acid of 0.6 normal concentration.

The effluent contains an aqueous solution of 2 - keto - d - gluconic acid of about 10% concentration. The said solution is evaporated under reduced pressure and subjected to lactone-enolization to obtain iso-ascorbic acid.

The quantity of isoascorbic acid recovered was equivalent to an oxidation yield of 93%.

The anion-exchange column 6 from which the product was displaced by means of hydrochloric acid, is then activated with a 2% sodium hydroxide solution.

2 - keto - d - gluconic acid being bonded in another anion-exchange column is eluted in the alkaline cycle by washing it with a 0.3 normal solution of ammonium hydroxide, yielding an aqueous solution of 2 - keto - d - gluconic acid ammonium salt in the eluate.

EXAMPLE 2

Process for the production of 2 - keto - 1 - gulonic acid by the fermentation of sorbitol.

A fermenter 1 shown in Fig. 4 and preparatory tanks 11 are filled with 5% sorbitol aqueous solution. 0.2% of glucose as bacteria nutrient and the same amount of yeast extract are added to the fermenter 1.

After adding calcium carbonate in an amount of 1/4 part of sorbitol in order to maintain a pH value of the fermenting solution in the range of 5—6, and a small amount of bacteria Genus Acetobacter, the content is stirred and actively aerated by means of a bubbler.

At first sorbitol is converted to 1 - sorbose which is oxidized to 2 - keto - L - gulonic acid which on being neutralized with calcium carbonate yields calcium 2 - keto - L - gulonate.

When the concentration of calcium 2 - keto - L - gulonate in the wort amounts to about 1 g per litre, the fermenting solution is continuously and uniformly drained out through a pipe to the filter 2 and simultaneously a freshly prepared solution is fed from the preparatory tank 11 through the sterilizer 3 into the fermenter 1.

In the fermenter a constant concentration of about 1 g per litre of calcium 2 - keto - L - gulonate is maintained. The pH of the solution is maintained in the range 5—6, due to the periodic addition of calcium carbonate to the fermenter.

In the meantime fermenting solution passes through the filter 2 to the cation exchange column battery 4 where the calcium cations in the solution are exchanged with hydrogen ions. The solution then passes through the receiver 5 to the anion-exchange column battery 6 where 2 - keto - 1 - gulonic acid is retained and the wort, containing other substances, passes to the receiver 7. The wort is pumped by means of a pump 9 to the preparatory tanks 11. The following substances are added to the wort in the tank; sorbitol in a quantity equivalent to the quantity of 2 - keto - 1 - gulonic acid being removed from the wort, the yeast extract and glucose in the quantity equivalent to compensate the loss in the wort to the previous level.

The solution flows continuously from the tanks 11 through a sterilizer and a heater 3 to the fermenter 1 wherein calcium carbonate is successively added in order to maintain the suitable pH at a temperature of 28—30°C.

In order to prevent the wort from microbiological contamination it was examined from time to time.

If such contamination occurs, the fermenter should be changed. However if sterile conditions are observed those events are rather rare. When, after a lapse of time the cation-exchange column battery became deactivated it was regenerated by washing with a 3% solution of hydrochloric acid.

When the anion-exchange column battery was saturated, the post-fermentation solution was passed through another anion-exchange column and the 2 - keto - L - gulonic acid was eluted with 2% hydrochloric acid from the feeder 12 so that an aqueous solution of 2 - keto - L - gulonic acid having a concentration of 9.5% was collected in receiver 8.

The anion-exchange column was reactivated by washing with a 2% solution of ammonium hydroxide.

After repeated saturation of the anion-exchange column with 2 - keto - L - gulonic acid, the product was eluted therefrom with a 0.5 normal solution of sodium hydroxide to yield an 8% solution of sodium 2 - keto - L - gulonate whilst simultaneously preparing the anion-exchange bed for further adsorbtion of the post-fermentation solution.

The obtained aqueous solution of 2 - keto - 1 - gulonic acid was evaporated under reduced pressure to yield a crystalline acid, having a melting point of 165.5—166°C.

The yield of the sorbitol oxidation was 82%.

EXAMPLE 3

Process for the production of lactic acid.

An aqueous sacchrose solution having a concentration of 15% was introduced into the fermenter 1 from preparatory tank 11,

After adding bacteria genus Lactobacillus delbruckii, about 3% of yeast extract together with malt sprouts as nutrients and calcium carbonate, into the fermenter, the temperature of the solution was raised to 50°C.

Then the solution was submitted to lactic fermentation and yielded quickly a high concentration of lactate.

When the concentration of lactate in the wort reached 2%, the fermenting solution was continuously drained off to the filter 2 and simultaneously a freshly prepared solution was fed from the preparatory tanks 11 through a sterilizer 3 into the fermenter 1.

In this way a constant concentration of lactate of about 1—2% was maintained. Additionally, the solution was kept at a pH of 4.7 to 6.0.

In the meantime, the fermenting solution passed through the filter 2, to the cation-exchange column battery 4 wherein calcium cations, included in the solution, were exchanged for hydrogen ions. Then the solution was passed through the receivers 5 to the anion-exchange column battery 6, where the lactic acid was retained whilst a saccharose solution together with other substances was passed to the receivers 7 and subsequently were fed by means of the pump 9 to the preparatory tanks 11 wherein the concentration of saccharose was increased to about 15%. Yeast extract together with malt sprouts were added as nutrients for bacteria.

The solution was continuously fed from the tanks 11 through a sterilizer and a heater 3 into the fermenter 1 wherein calcium carbonate was added stepwise, in order to maintain a constant pH therein at a temperature of about 50°C.

From tme to time microbiological and chemical examination of the wort were made in order to prevent its contamination.

If such contamination occurs, the fermenter should be changed. However if sterile conditions are observed, those events are rather rare.

When after a lapse of time, the cation-exchange column battery became deactivated, it was regenerated by washing with a 3% solution of hydrochloric acid.

When the anion-exchange column battery was saturated the fermenting solution eluted through a fresh battery. Lactic acid was eluted from the saturated battery with a 7.5% solution of mineral acid, flowing from feeder 12 so yielding in the receiver 8 as final product lactic acid having a concentration of about 18%.

The yield of the product in relation to the starting saccharose was 92%.

The anion-exchange column was washed with a 2% solution of sodium hydroxide and water in order to prepare it for a new batch of lactic acid.

All these operations were performed with application of interstage evacuation of the ion-exchange bed.

The obtained solution of the lactic acid shows very high purity and neither changes its colour nor transparency during a long storage.

WHAT WE CLAIM IS:—

1. A method of controlling the oxidation of a carbohydrate or polyhydric alcohol comprising treating a feedstock containing the carbohydrate or polyhydric alcohol with an oxidising agent to form a reaction mixture containing a monocarboxylic acid; and removing the monocarboxylic acid; during formation thereof so that the feedstock is maintained in the reaction mixture at a concentration greater than that of the monocarboxylic acid.

2. A method according to claim 1 wherein the concentration of the acid is maintained at a predetermined level related to the oxidation-reduction equipotential point.

3. A method according to claim 1 or 2 wherein the acid is removed by means of ion-exchange electro-dialysis or sorption.

4. A method according to claim 1 or 2 or 3, comprising introducing a small portion of an oxidising agent into a reactor into which the feedstock is continuously fed, to form a reaction mixture, passing part of the reaction mixture through an ion-exchange system, wherein the acidic product is retained while unoxidised feedstock passes to the effluent which is recycled into the reactor, and recovering the product from the ion-exchange unit by regerenation in a known manner, to yield a solution of the acid or its salt.

5. A method according to any preceding claim wherein the oxidising agent is selected from nitric acid, nitrous acid, nitrogen oxides, chlorine, bromine, oxidising halogeno acids and salts thereof, transition metal salts, hydrogen peroxide with a suitable catalyst, oxygen, air, ozone, gaseous mixtures containing oxygen or ozone optionally in the presence of a catalyst, enzymes and microbiological oxidising agents.

6. A method according to claim 5 wherein the microbiological oxidising agent is Acetobacter, Pseudomonas or Lactobacillus.

7. A method according to any one of claims 1 to 4 wherein the oxidation is effected electrochemically optionally in the presence of an oxygen-bearing medium.

8. A method according to any preceding claim wherein the carbohydrate or polyhydric alcohol is selected from ketohexoses, aldohexoses, aldopentoses, reducing disaccharides, starch, cellulose hydrolysates and molasses.

9. A method according to any preceding claim with reference to any one of the Examples.

10. A monocarboxylic acid whenever prepared according to any one of claims 1 to 9.

11. Apparatus when used for controlling

the oxidation of a feedstock of a polyhydric alcohol or carbohydrate by a method according to any of claims 1 to 9 substantially as hereinbefore described with reference to any 5 one of Figs. 2, 3 or 4.

Fig.1

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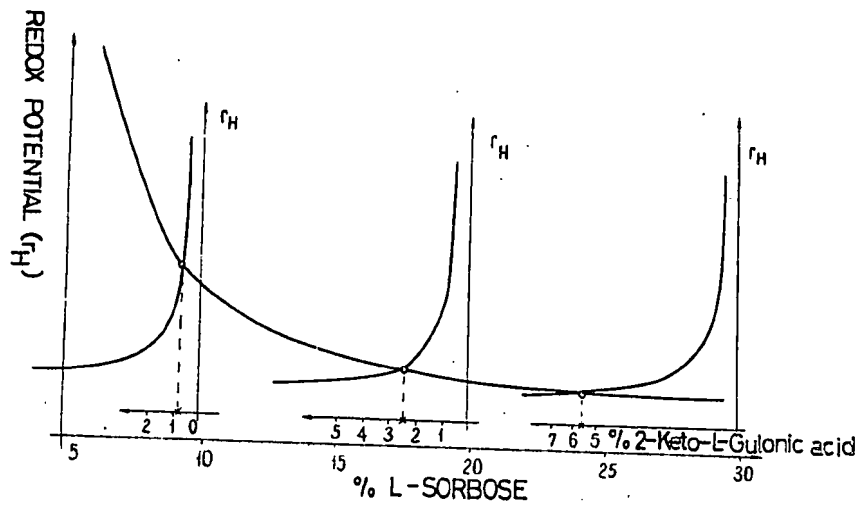
4   SHEETS   *This drawing is a reproduction of*
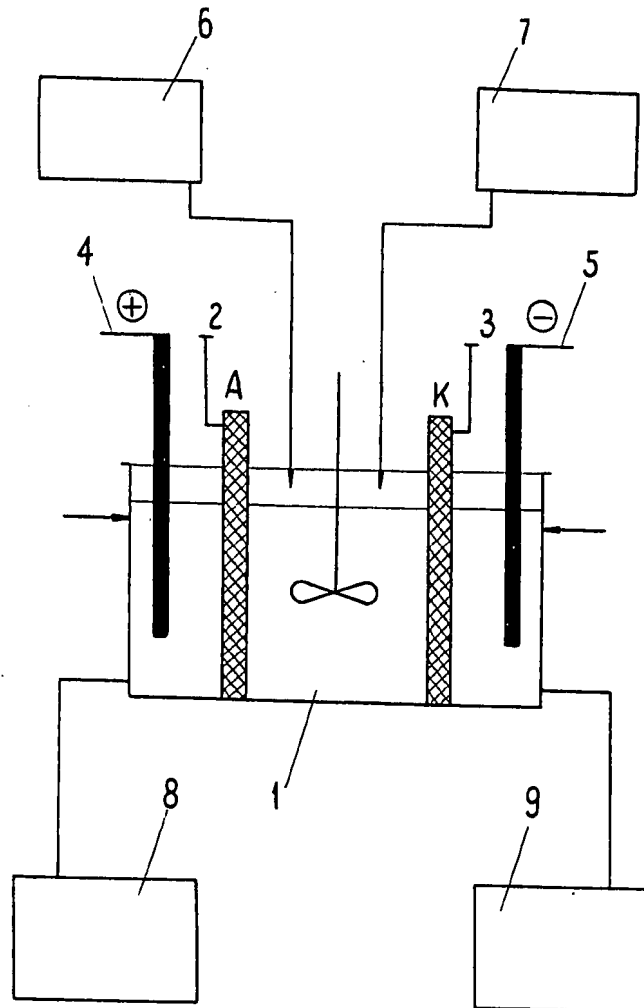*the Original on a reduced scale*
Sheet 2

Fig.2

Fig.3

Fig. 4